PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 38, NOS. 1–2, PP. 75–80 (1994)

MONTE CARLO CALCULATIONS: DIFFUSION IN ZEOLITES

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Received: June 28, 1994

Abstract

The objective of this study is to estimate the diffusivities of single and multicomponent systems as a function of temperature, concentration and parameters of the zeolite framework.

Keywords: diffusion in zeolites, Monte Carlo calculations.

Zeolites play an important role as catalysts, ion exchangers and sorbents (WEITKAMP et al, 1992). As the diameters of molecules and pores in zeolites are of comparable size the diffusion in zeolites is restricted. This still poorly understood type of diffusion is called configurational diffusion. Unlike diffusivities for gaseous and Knudsen diffusion, diffusivities in zeolites cannot be expressed by simple formulae (XIAO and WEI, 1992a).

The simulation is based on a random walk model, i. e, a sequence of uncorrelated activated jumps of molecules in a lattice (KÄRGER and RUTHVEN, 1992; GERMANUS, 1986). The lattice consists of four different types of lattice elements: inaccessible zeolite framework, free intracrystalline space, active sites and potential barriers at the transition from the cage (intersection) to the channel. During one time step in a Monte Carlo (MC) simulation each molecule is chosen once at random. Then the direction of movement is determined randomly with equal probability. The molecule moves in the initial direction as long as one of the following events occurs (*Fig. 1*):

- The collision with framework, other molecules, or clusters of molecules stops the movement immediately (inelastic impact).
- A molecule residing on an active site is hindered from jumping with a specific probability. Also a chemical reaction can take place on active sites again with a certain probability, which depends on the reaction rate constants.

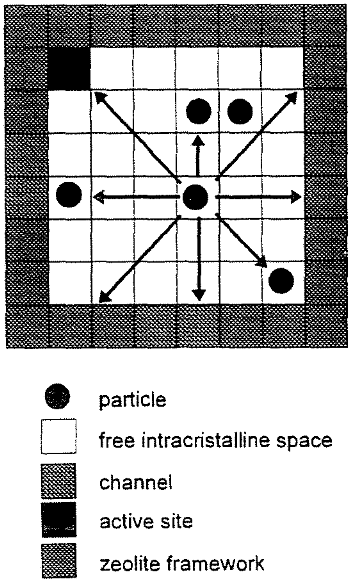

Fig. 1. Movement of a molecule in a discrete lattice structure

- If a diffusing molecule tries to leave a cage (intersection), it has to overcome a potential barrier. If the jump is successful, the molecule continues moving in the initial direction as long as one of the former events occurs.

As a first approximation the activation energy, $\Delta\phi$, is estimated by the (12,6)-Lennard-Jones potential of the interaction between the molecule and the oxygen atoms of the zeolite framework

$$\Delta\phi = \sum_{c} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{1}$$

(σ: Lennard-Jones length constant, ε: Lennard-Jones energy constant, r: distance between the nuclei of the molecule and the center of the oxygen atoms). The Lennard-Jones parameters are determined either from transport properties or from detailed measurements of the deviations from the ideal gas law (Reid et al, 1987). The distance between the diffusing molecule and the interacting oxygen atoms, r, depends on the intersection diameter and channel diameter, respectively. Only first neighbours are considered as interacting molecules, no interaction between molecules is included.

The mean lifetime on an adsorption site, τ, is approximated by the frequency, ν, of a harmonic oscillator

$$\nu = \sqrt{\frac{\Delta\phi}{2mL^2}}\,, \tag{2}$$

(m: molecular mass, L: jump length). Therefore, the time for one Monte Carlo step can be calculated by

$$\tau = \frac{1}{6\nu} e^{\frac{\Delta\Phi}{kT}}\,, \tag{3}$$

(k: Boltzmann constant, T: temperature) (KÄRGER et al, 1980). The order of magnitude of this time step is in agreement with results of Molecular Dynamics simulations for the mean site residence time (VAN TASSEL et al). The probability of overcoming the potential barrier of an active site or window barrier is given by the well-known Boltzmann distribution. Finally, the jump length is correlated with the known dimensions of a unit cell. Note that there is no adjustable parameter in this approach.

The self-diffusivity, D_{Self}, is calculated by the Einstein relation (KÄRGER and RUTHVEN, 1992)

$$\langle \vec{r}^{\,2}(t) \rangle = \int \frac{e^{\frac{-\vec{r}^{\,2}}{4Dt}}}{(4\pi D_{\mathrm{Self}} t)^{\frac{3}{2}}} \vec{r}^{\,2} \mathrm{d}\vec{r} = 6 D_{\mathrm{Self}} t\,, \tag{4}$$

$\left(\langle \vec{r}^{\,2}(t) \rangle\right.$: mean square displacement, t: time$\left.\right)$ that provide a direct correlation between diffusivity, as defined by Fick's first law, and the time dependence of the mean square displacement. For discrete time steps follows

$$D_{\mathrm{Self}} = \lim_{t\to\infty} \frac{\langle \vec{r}^{\,2} \rangle}{6t} = \lim_{N\to\infty} \frac{\langle \vec{r}^{\,2} \rangle}{6N\tau}\,, \tag{5}$$

(N: number of Monte Carlo steps, τ: time step).

Detailed three dimensional modelling of the zeolite framework structure offers several advantages. First, the channel system and cage dimensions can be modelled in a realistic way. Second, the mutual interaction between diffusing molecules can be investigated. Third, pore blocking, e. g. caused by coke deposition, can be simulated in a simple way. Application of a regular composed lattice unit structure makes it possible to generate any size of a periodic lattice.

In this study a three dimensional model of the ZSM-5 pore structure is analysed. The framework structure, depicted in *Fig. 2,* consists of

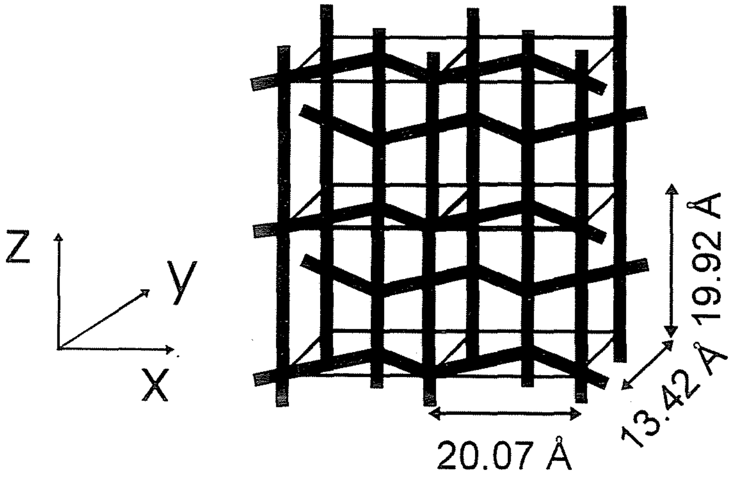

Fig. 2. Channel structure of ZSM-5 with dimensions of the unit cell

straight channels with elliptical cross-section and zig-zag-shaped channels with circular cross-section (OLSON et al, 1981).

One of the most studied sorbate in silicalite has been benzene. Silicalite has the same framework structure as ZSM-5, but a very high Si/Al ratio. *Fig. 3* shows the limiting diffusivity, D_0, which is at low concentration comparable to the self-diffusivity, D_{Self}, as a function of temperature. The open symbols connected with lines are the results of the Monte Carlo simulation. The filled symbols show experimental data of different measuring techniques found in literature (KÄRGER and RUTHVEN, 1992, XIAO and WEI, 1992b). There is a good agreement between calculated and experimental diffusivities. Moreover, the channel structure of ZSM-5 reveals a diffusional anisotropy at low concentration of sorbates, which is also confirmed by Molecular Dynamic simulations (DEMONTIS et al, 1992).

Due to the molecular size of benzene the mutual interaction with the zeolite framework is very strong which results in very low diffusivities.

In conclusion, our results are very encouraging, though we used a model with very simplifying assumptions. In this approach, the diffusivities calculated are independent of any experimental adsorption kinetic data. Thus, on the basis of the Lennard-Jones parameters, molecular parameters, and the zeolite geometry only, the model should be able to predict diffusivities reasonably well for other zeolite sorbate systems. The agreement of predicted diffusivities in dependence of temperature and intracrystalline concentration for other hydrocarbons is quite good. However, of great in-

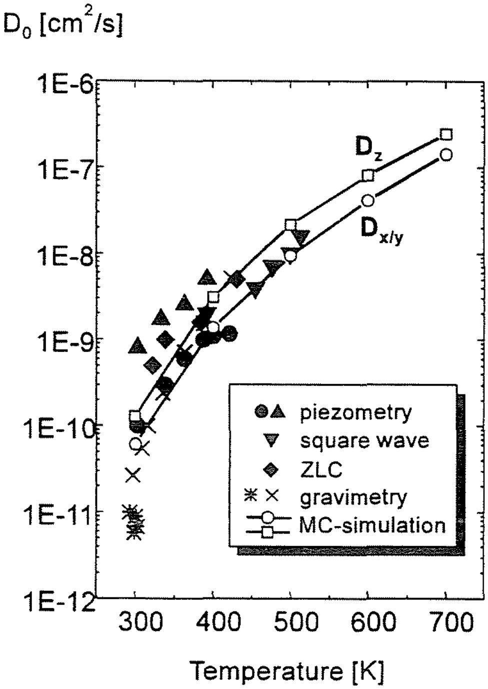

Fig. 3. Temperature dependence of the limiting diffusivity for benzene in silicalite

terest is the interplay of diffusion and reaction with size and shape selective behaviour. Our future investigations will be concentrated on this topic.

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